Summary of Research for NASA Cooperative Agreement NCC-1-262 for the period June 1, 1997 to May 31, 1999

Title: **FLIGHT VALIDATION OF ATOMIC OXYGEN RESISTANT POLYMERS**

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Because of its high reactivity, atomic oxygen causes surface erosion on polymeric materials, although the reaction efficiency depends on the chemical structure of the polymer[1]. We have found an organotin compound, bis(triphenyltin) oxide (BTO), which has an unusually high solubility in solutions of a number of commercial high performance polymers. Films of these polymers containing BTO showed a substantial reduction in erosion by atomic oxygen when compared with films of the pure material. Analysis has shown that in the presence of atomic oxygen, erosion of the exposed surfaces of the BTO-containing films leaves a residual protective tin oxide coating[2]. Since the additive is uniformly distributed throughout the polymeric material, any break or puncture in the protective coating is "healed" by the material below. Samples were exposed to the environment of the low earth orbit (LEO) on two Space Shuttle flights, STS-46, in June of 1992, and STS-51 in September of 1993. The analysis of these samples has been reported previously[3]. For both flights, the samples were small (1.3 cm and 1.9 cm respectively) thus limiting the scope of analysis.

In the research under this cooperative agreement, films of a polyetherimide, were exposed to the LEO environment on Space Shuttle flight STS-85 in August of 1997 as part of the Evaluation of Space Environment and Effects on Materials (ESEM) experiment. The polyetherimide chosen is available commercially as Ultem, registered to the General Electric Company. Films of pure Ultem, Ultem with 10% BTO by mass, and Ultem with 20% BTO by mass were exposed in the ram direction for 40 hours during STS-85. Ultem has a T_g of 215°C and is soluble in common chlorinated solvents. Granules of the polymer were dried at 120° C, but otherwise were used as received. Films were cast on a glass plate from a solution of the polymer in a 60/40 (w/w) mixture of chloroform and 1,1,2,2-tetrachloroethane. The plate was placed in a dust-free box for at least 24 hours to allow much of the solvent to evaporate, and then was moved to a vacuum oven and slowly heated from 20 to 220° C over a period of two weeks to completely remove all solvent. Each exposed sample was 7.6 cm long and 2.2 cm wide and about 0.025 mm thick. The structures of Ultem and bis(triphenyltin) oxide are shown in Figure 1.

The exposed and control samples were analyzed by X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), electron paramagnetic resonance spectroscopy (EPR), as well as for mass loss. The samples were weighed on a Mettler H20T balance before and after the space exposure. Subsequently, pieces of the exposed and control samples 1.3 cm by 2.2 cm were cut for XPS analysis at the Surface Analysis Laboratory in Blacksburg Virgina on a Perkin Elmer 5400 instrument. Additional pieces, 1 cm by 0.5 cm, were cut for FTIR analysis on a Nicolet DSB-20 spectrometer. The remainder of the each of the exposed and control samples was carefully rolled and inserted into the end of an EPR tube for analysis on a Perkin Elmer E-Line Century Series instrument.

Mass measurements showed that the pure Ultem sample lost significantly more mass than the two BTO-containing samples. Also, the reaction efficiencies for the BTO-containing samples was much lower that for the pure Ultem sample. The reaction efficiency is equal to the mass loss divided by the product of the density, area, and atomic oxygen fluence. The atomic oxygen (AO) fluence was measured by mass loss of a Kapton film and was determined to be 8.6×10^{19} AO

atoms/cm^2. These results are shown in Table 1.

Table 1. Mass Loss and Reaction Efficiency Data

Sample	Mass Loss	Reaction Efficiency
Pure Ultem	6.11 mg	3.3×10^{-24} cm^3/atom
Ultem/10% BTO	3.10 mg	1.7×10^{-24} cm^3/atom
Ultem/20% BTO	2.02 mg	1.1×10^{-24} cm^3/atom

X-ray photoelectric spectroscopy revealed that significant surface chemistry occurred during the LEO exposure, particularly for the BTO-containing samples. Figures 2 and 3 compare the XPS survey spectra of the control and exposed samples of the films containing 10 and 20% BTO. The carbon 1s peak is diminished in the exposed samples, but the tin 3d peaks are greatly enhanced as is the oxygen 1s peak. This indicates that the predominant species on the surface are tin and oxygen, presumably in the form of a tin oxide compound. These can be compared with Figure 4 which shows the XPS survey spectra of the control and exposed samples of the pure Ultem film and revealing much less dramatic changes on exposure to the LEO environment. A detailed analysis of the carbon 1s peak for the Ultem/10% BTO control sample, shown in Figure 5, reveals that most of the surface carbon atoms are bonded to other carbon or hydrogen atoms so that the binding energy (BE) of the 1s electron is 285 eV. The remainder of the carbon atoms are singly bonded to an oxygen atom (BE = 286.5 eV) or doubly bonded to an oxygen atom (BE = 288 to 289 eV). In the exposed sample shown in Figure 6, however, the surface carbon atoms have two additional binding energies. One at 283.6 eV, characteristic of a carbon-metal bond, and another at 289.8 eV characteristic of a carbon atom bonded to three oxygen atoms. These data are summarized in Table 2.

Table 2 Binding energies of the Carbon 1s electrons in Ultem/10%BTO Samples

Peak Position	% of Total for Control	% of Total for Exposed
289.8		5.8
288.0 - 288.6	9.1	9.6
286.5	17.0	15.7
285.0	73.9	43.0
283.6		25.9

It appears that much of the surface carbon in the exposed sample is bonded to tin, presumably as BTO.

The results of FTIR analysis reveal a reduction of intensity in the spectra of the exposed samples, but no noticeable change in relative peak heights. The decrease in intensity is probably due to the diffuse surface which is visibly apparent on the exposed samples. This is illustrated in Figures 7 and 8 for the pure Ultem and Ultem/10% BTO samples.

Analysis by EPR revealed that all exposed samples had a greater number of radicals per gram than did the corresponding control samples. At least two different kinds of radical were present in all samples, a relatively short-lived species which decays in 3 to 4 weeks, and a long-lived species which was still present after 16 weeks. The short-lived species probably came from the process of rolling the samples into the EPR tube. The long-lived species is probably inherent in the material. In addition, exposure to high energy UV radiation in the LEO could cause increased radical formation. However, the exposed samples had more of both kinds of radical than the controls. It is not clear why there is an increase in the short-lived radicals in the exposed samples since the EPR measurements were begun several months after the samples were returned from space. Figures 9 and 10 illustrate these EPR data. Figure 9 is one differential curve for the Ultem/20% BTO samples, while Figure 10 summarizes the double integral data over time for the same samples. The double integral value is proportional to the number of radicals present.

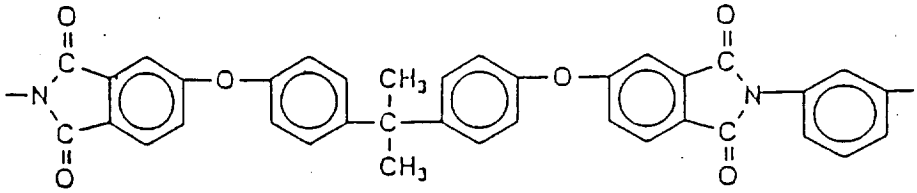
The presence of bis(triphenyltin) oxide in films of a polyetherimide reduces the erosion due to atomic oxygen in the low-earth orbit. An enhancement of tin and oxygen on the surface of exposed samples is clearly shown by XPS analysis. The reason for the increase in radical formation in the exposed samples is not presently known.

References

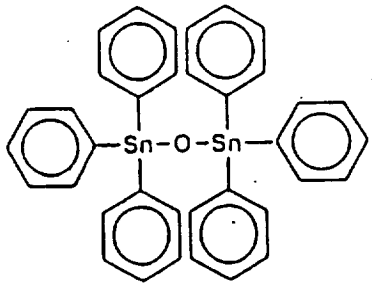
1. W. S. Slemp, B. Santos-Mason, G. F. Sykes, Jr.,and W. G. Witte, Jr., "Effects of STS-8 Atomic Oxygen Exposure on Composites, Polymer Films, and Coatings," **AIAA-85-0421**, *AIAA 23rd Aerospace Science Meeting*, Jan. 1985.

2. R. L. Kiefer, R. A. Orwoll, E. C. Aquino, A. C. Pierce, and S. A. Thibeault, "Reduced Erosion by Atomic Oxygen of a Polyetherimide Containing Bis(triphenyltin) Oxide", *Pacific Polymer Conference Preprints*, **3**, 407 (1993).

3. R. L. Kiefer, R. A. Orwoll, E. C. Aquino, A. C. Pierce, M. B. Glasgow, and S. A. Thibeault, "The Effects of Atomic Oxygen on Polymer Films Containing Bis(triphenyltin) Oxide", *Polymer Degradation and Stability*, **57**, 219 (1997).



POLYETHERIMIDE (ULTEM)



BIS(TRIPHENYLTIN) OXIDE (BTO)

Fig. 1 The structures of Ultem and BTO.

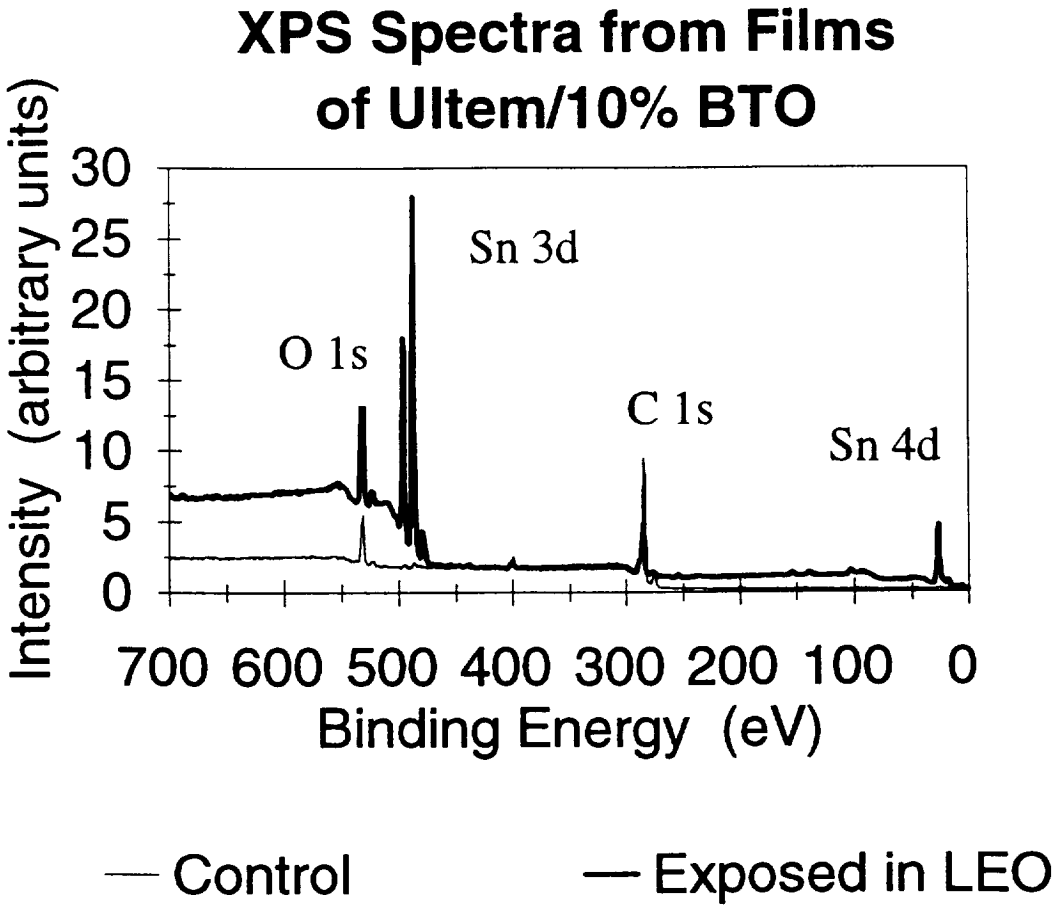


Fig. 2 The XPS survey spectra from films of Ultem/10% BTO.

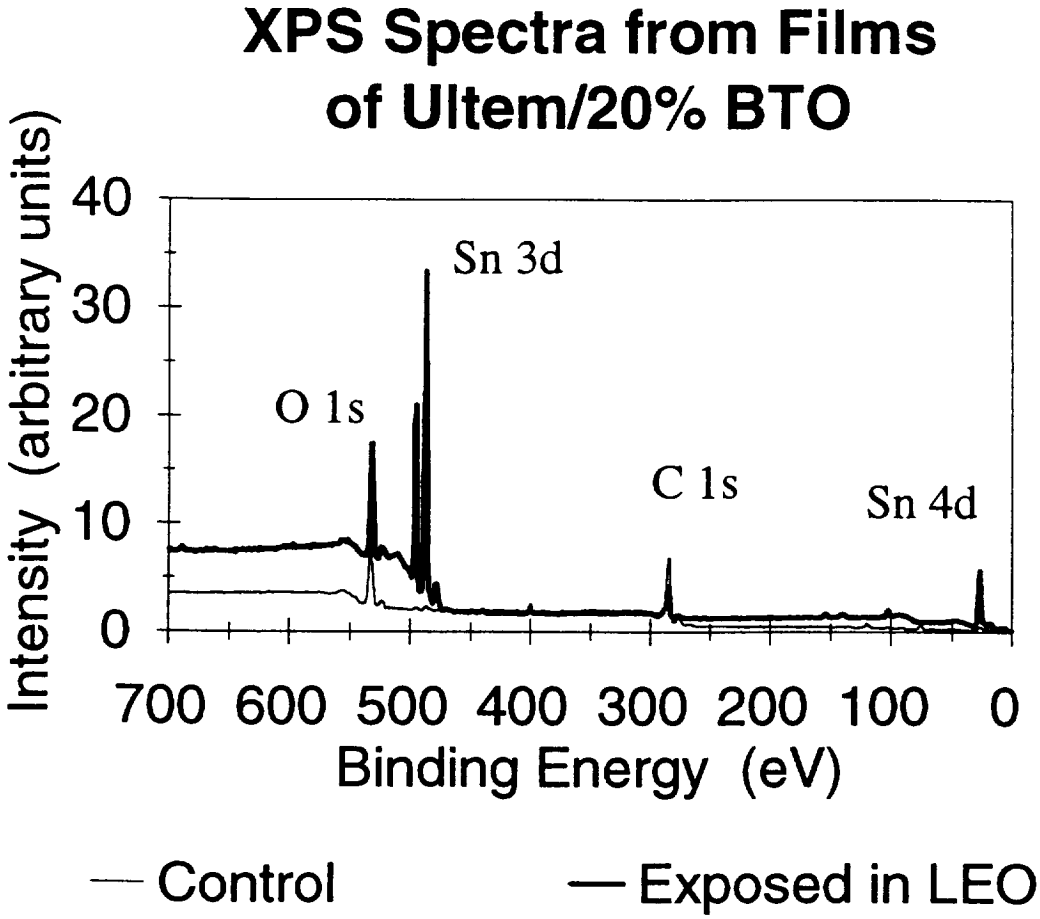


Fig. 3 The XPS survey spectra from films of Ultem/20% BTO.

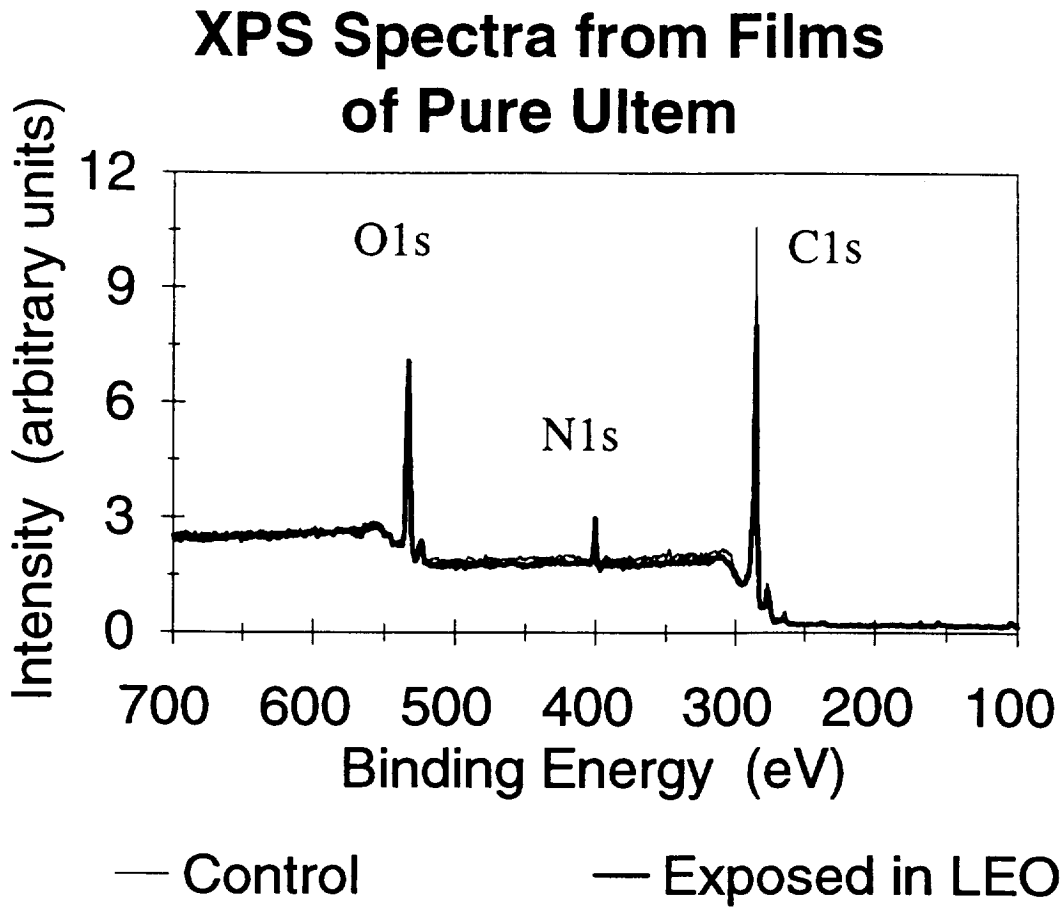


Fig. 4 The XPS survey spectra from films of pure Ultem.

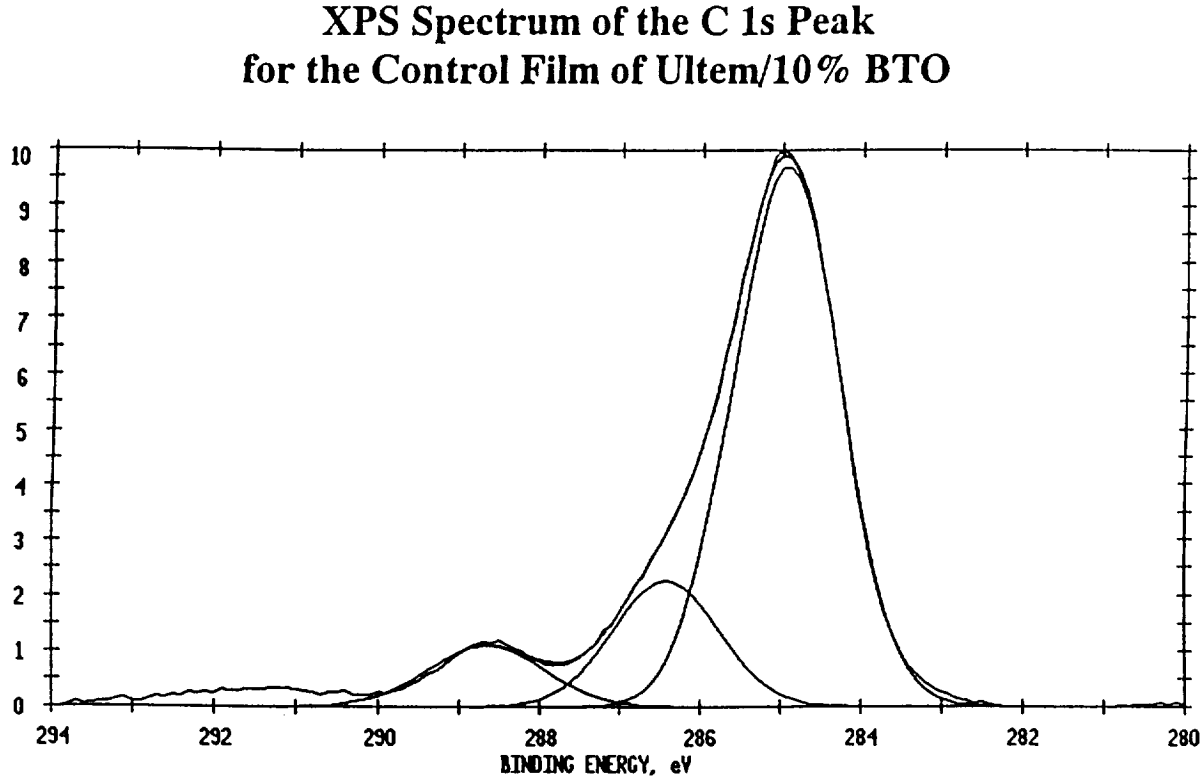


Fig. 5 The XPS spectrum of the carbon 1s peak for the Ultem/10% BTO control film.

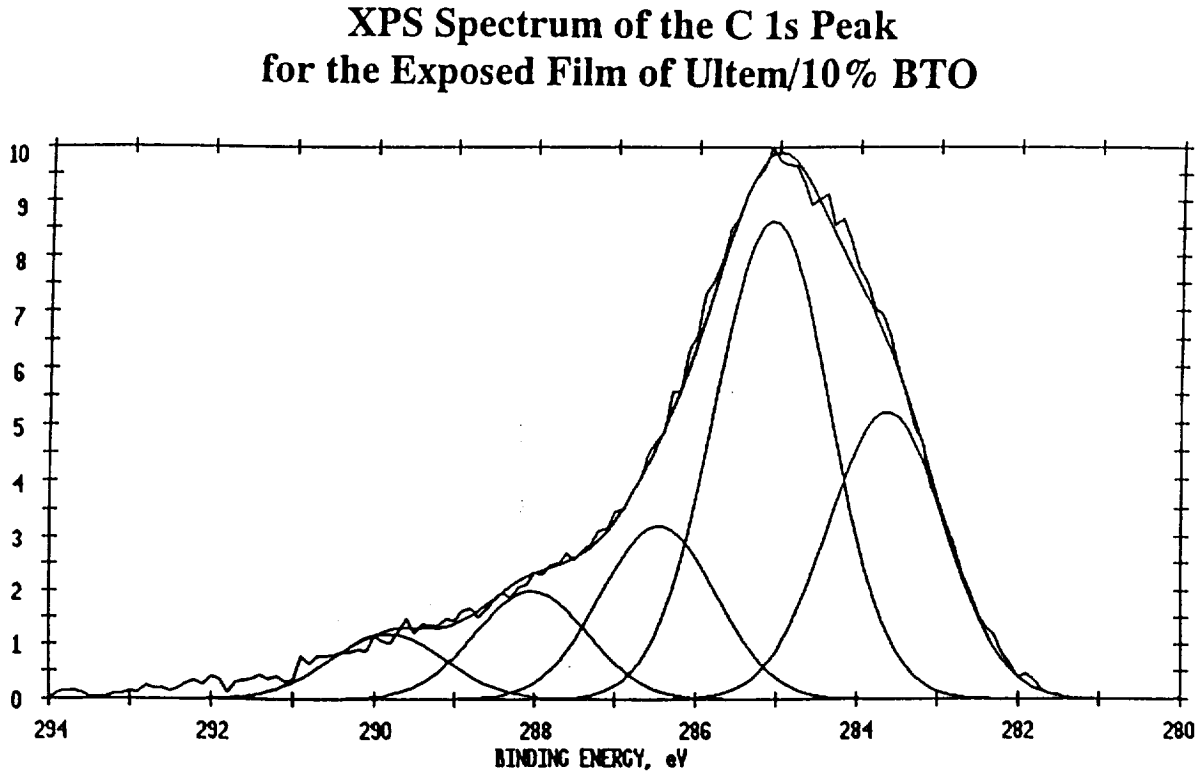


Fig. 6 The XPS spectrum of the carbon 1s peak for the Ultem/10% BTO film exposed in LEO.

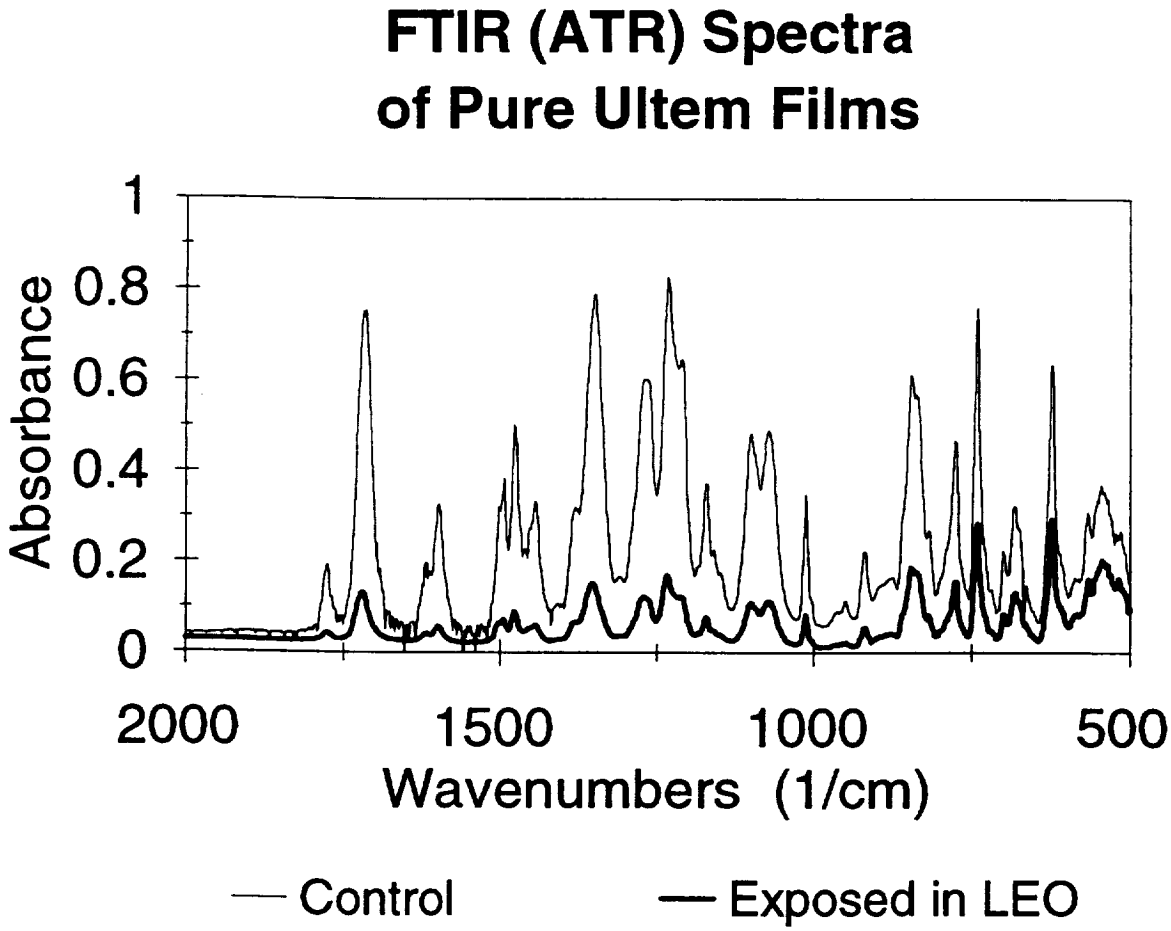


Fig. 7 The FTIR attenuated total reflectance spectra of pure ultem films.

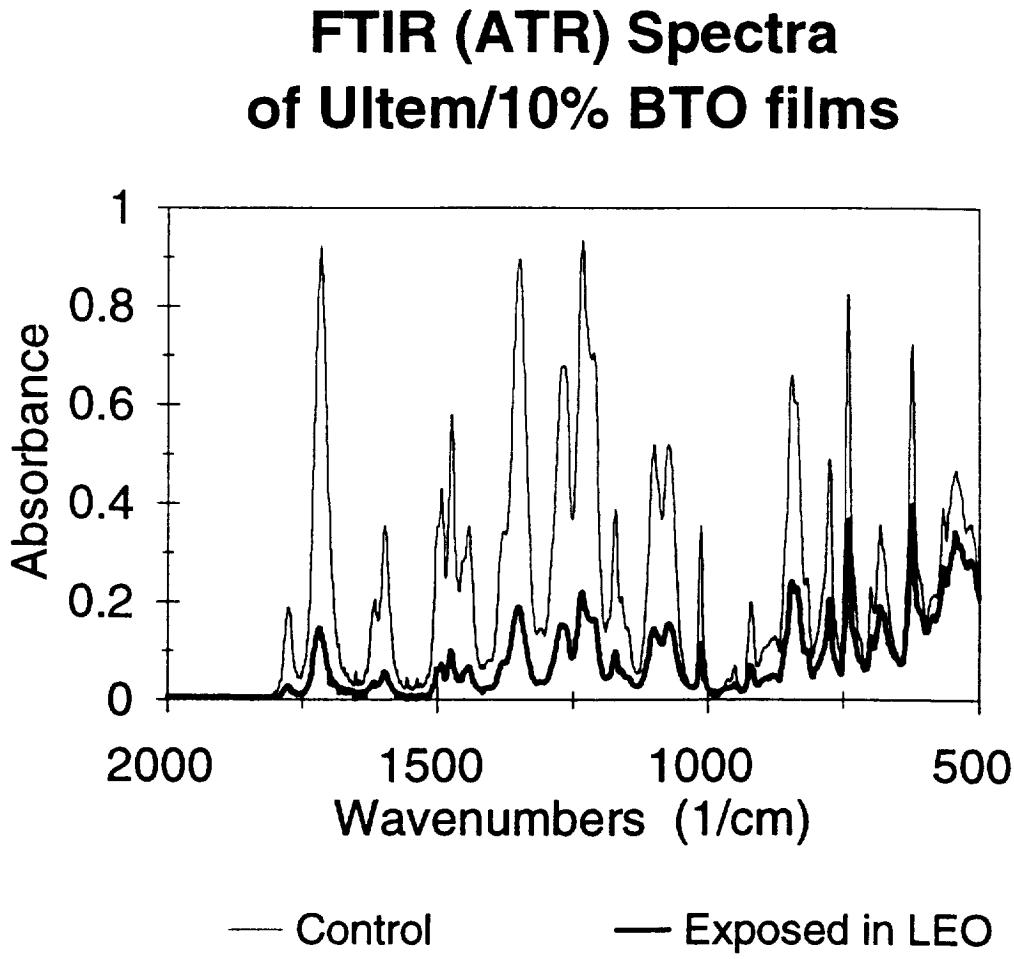


Fig. 8 The FTIR attenuated total reflectance spectra of Ultem/10% BTO films.

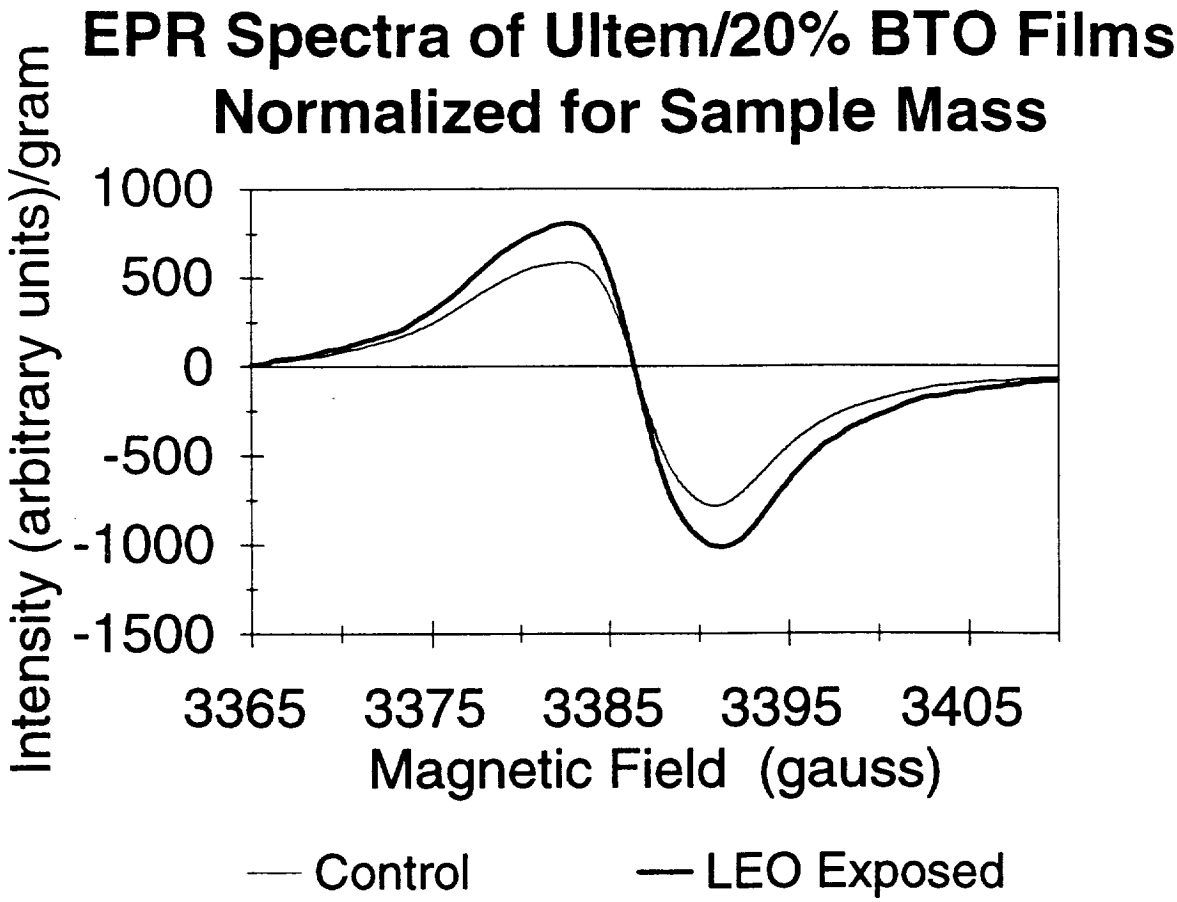


Fig. 9 EPR differential spectra of Ultem/20% BTO films nornalized for sample mass.

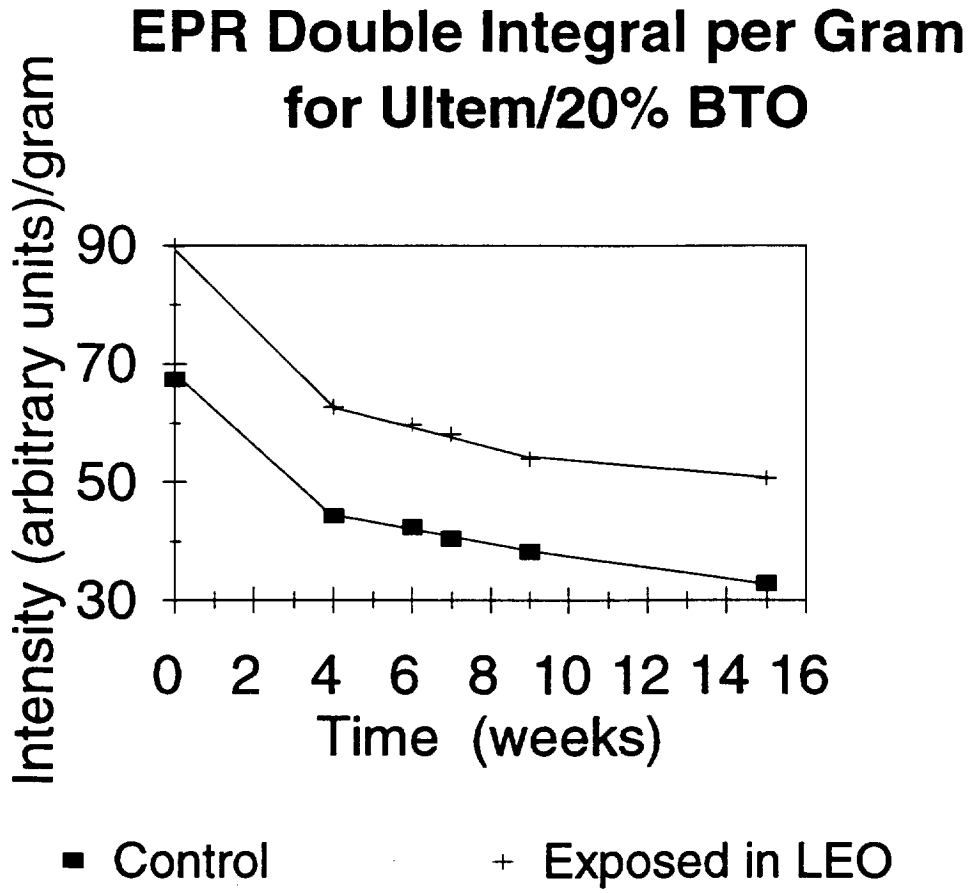


Fig. 10 EPR double integral data per gram for the Ultem/20% BTO samples over the time of measurement.